PATENTS ACT, 1964

COMPLETE SPECIFICATION

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DENTAL MATERIALS

OPEN TO PUBLIC INSPECTION UNDER SECTION 28 AND RULE 23 ENT. NO. 1691 OF 23.9.92

APPLICATION NO. 920833

SPECIFICATION FILED 13/3/92

BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of the Federal Republic of Germany, at Leverkusen, Federal Republic of Germany.

The invention relates to dental materials, their preparation and their use.

Dental materials can be employed, for example, for the production of false teeth, crowns, bridges, inlays, overlays, tooth fillings and dental varnishes.

The preparation of dental materials based on polymeric-(meth)acrylates is known. Thus, for example, materials which contain polymethyl methacrylate bead polymers as the powder component and mixtures of methyl methacrylate and ethylene glycol dimethacrylate are prepared; the mixtures in general harden by free radical polymerisation while being shaped (Ullmann's Encyclopedia of Industrial Chemistry, Fifth Edition, Volume A8, page 277 et seq. VCH Verlagsgesellschaft m.b.H., Weinheim 1987).

US 4,396,377 proposes dental materials for the production of false teeth which contain (in addition to non-crosslinked) crosslinked polymethyl methacrylate as the powder. The conventional mixture of methyl methacrylate and a crosslinking agent, such as ethylene glycol dimethacrylate, is used as the monomer liquid. Dental materials according to US 4,396,377 have the following composition:

0-50% of non-crosslinked polymer
10-70% of crosslinked polymer
20-66% of monomer (which does not act as a crosslinking

agent)
7-27% of crosslinking agent

EP-A 59,525 describes similar materials to the patent specification cited above. The materials claimed have the following composition:

0-50% of non-crosslinked polymer
10-70% of crosslinked polymer
2-30% of monomer (which does not act as a crosslinking agent)
20-70% of crosslinking agent

EP-A 346,707 has disclosed dental materials for the production of false teeth in which exclusively or predominantly crosslinking agents are used as the monomer liquid and exclusively crosslinked polymer having particular swelling properties is used as the polymer component. These dental materials have the following composition:

5-35% of crosslinked polymer
0-40% of monomer (which does not act as a crosslinking agent)
40-90% of crosslinking agent.

DE-A 2,403,211 describes dental compositions which contain fillers and are characterised in that they contain exclusively microfine silicon dioxide as the filler and bis-GMA or specific urethane methacrylates obtained by reaction of diisocyanates with hydroxyalkyl

methacrylates as the monomer.

Dental materials containing

a) 5 to 30 parts by weight of an organic filler consisting of polymeric crosslinked (meth)acrylates having a particle size in the range from 0.001 to 100 µm, a degree of swelling of 50 to 2000% by weight and a degree of crosslinking of 1 to 100% by weight, in each case based on the polymer,

b) 40 to 80 parts by weight of (meth)acrylates which can form crosslinkings,

c) 0 to 40 parts by weight of (meth)acrylates which cannot form crosslinkings,

d) 10 to 40 parts by weight of a silanised inorganic filler having an average particle size of 0.005 to 5 µm and

e) 0.1 to 10% by weight of one or more additives,

have been found.

The dental materials according to the invention are distinguished, surprisingly, by a particularly good hardness and high rigidity. They can be processed to very thin layers.

They can be polished very well and give hard, high-gloss surfaces by this procedure. The wear resistance of the dental materials according to the invention is very high. After addition of pigments, an outstanding similarity to the appearance of natural teeth is achieved.

Component (a)

Organic fillers in the context of the invention are polymeric crosslinked (meth)acrylates having a particle size in the range from 0.001 to 100 µm, preferably 0.01 to 10 µm, a degree of swelling of 50 to 2000% by weight and a degree of crosslinking of 1 to 100% by weight, preferably 50 to 100% by weight, in each case based on the polymer.

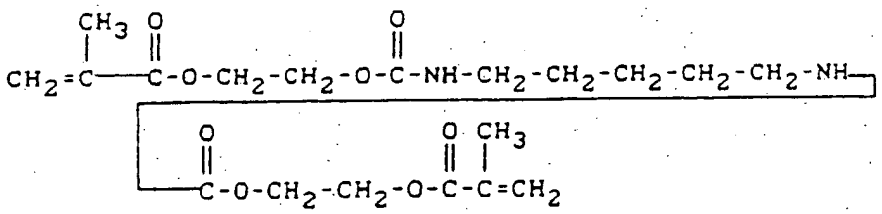
The content of methacrylic acid esters which can form crosslinkings, based on the polymer, is defined here as the degree of crosslinking.

Monomeric (meth)acrylates of the organic fillers which form crosslinkings are (meth)acrylates having two or more, preferably 2 to 4, polymerisable double bonds in the molecule.

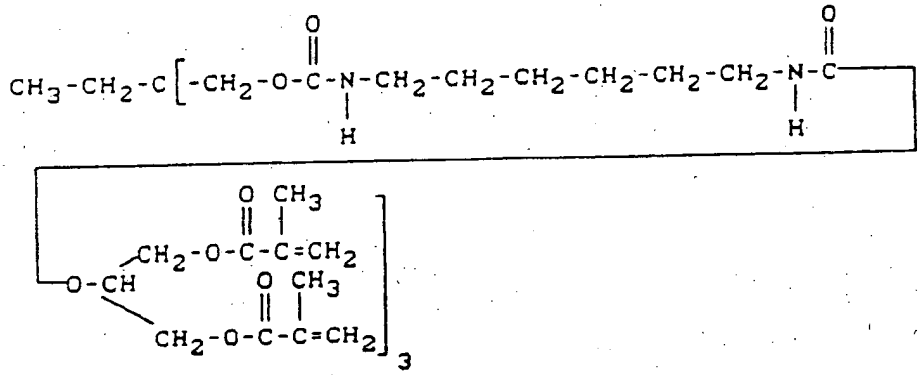
Examples which may be mentioned of monomeric (meth)acrylates which form crosslinkings are:

ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, glycerol dimethacrylate, glycerol trimethacrylate, trimethylol-

propane trimethacrylate, pentaerythritol dimethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, derivatives of bisphenol A, such as bisphenol A dimethacrylate and bisphenol A diglycidyl dimethacrylate, urethane methacrylates which can be prepared by reaction of diisocyanates and hydroxyalkyl methacrylates, such as



and reaction products of polyols, diisocyanates and hydroxyalkyl methacrylates (DE-A 3,703,080, DE-A 3,703,130 and DE-A 3,703,120), such as, for example,



Preferred monomeric (meth)acrylates are those which form

crosslinkings, such as:
ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate and glycerol dimethacrylate.

Examples which may be mentioned of monomeric (meth)acrylates of the fillers which do not form crosslinkings are:

C_1-C_{12}-, preferably C_1-C_4-alkyl methacrylates, such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate and t-butyl methacrylate,
hydroxyalkyl(C_1-C_4) methacrylates, such as 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, diethylene glycol monomethacrylate and triethylene glycol monomethacrylate, and alkoxy(C_1-C_4)ethyl methacrylate, such as 2-methoxyethyl methacrylate, 3-methoxybutyl methacrylate and ethyltriglycol methacrylate.

Preferred monomeric (meth)acrylates which do not form crosslinkings are, for example:

methyl methacrylate, ethyl methacrylate and 2-hydroxyethyl methacrylate.

The monomeric (meth)acrylates are known per se and can be prepared, for example, by reaction of (meth)acryloyl chloride with the corresponding alcohols.

It is of course possible for the (meth)acrylates,

according to the invention, of the organic fillers to form copolymers with other monomers. Examples which may be mentioned here are copolymers with styrene, α-methylstyrene, acrylonitrile and vinyl acetate. In these cases, the content of the comonomer is 0 to 40, preferably 0 to 20% by weight, based on the polymer.

The degree of swelling is understood as meaning the uptake capacity of the poly(meth)acrylates according to the invention for liquid. The degree of swelling is measured by the uptake capacity for tetrahydrofuran at 20°C. The poly(meth)acrylates according to the invention have a swelling capacity of 50 to 2000% by weight, preferably 100 to 1000% by weight, based on the polymer.

The organic fillers according to the invention in general have an average particle diameter of 0.001 to 100 μm, preferably 0.01 to 10 μm.

The organic fillers according to the invention preferably have a gel content of 5 to 100% by weight, preferably 95 to 100% by weight, based on the polymer. In the context of the present invention, the gel content is understood as meaning, according to the definition, the content of the polymer which is not soluble in tetrahydrofuran as the solvent at 20°C. The gel content is a parameter for the actual crosslinking which has occurred.

The organic fillers according to the invention preferably have an active surface area of 10 to 600 m^2/g, preferably

50 to 300 m^2/g, measured by the BET method.

Organic fillers according to the invention having a particle size of about 5 - 100 μm can be synthesised by the process of suspension polymerisation.

Preferred organic fillers according to the invention having a particle size of 0.001 to 10 μm can be prepared by polymerising (meth)acrylates which form crosslinkings, and if appropriate (meth)acrylates which do not form crosslinkings, as the monomer, and if appropriate other comonomers in the presence of an organic solvent having a solubility parameter of 8 to 15 $[cal^{0.5}cm^{-1.5}]$, the monomer content of the (meth)acrylates which form crosslinkings being 50 to 100% by weight.

Organic solvents can be defined by the so-called solubility parameter (H.G. Elias, Makromoleküle, p. 192-196 (1981)). Solvents having a parameter of 8 to 15 $[cal^{0.5}cm^{-1.5}]$, preferably 8.5 to 12 $[cal^{0.5}cm^{-1.5}]$ are used for the process according to the invention.

The following solvents may be mentioned as examples:

amyl acetate, tetrachloroethane, toluene, ethyl acetate, tetrahydrofuran, benzene, chloroform, methylene chloride, methyl chloride, acetone, 2-butanone and tert.-butanol.

The amount of solvent in relation to the monomeric (meth)acrylates is in the range from 1:1 to 1:100,

preferably 1:2 to 1:20.

The polymerisation process is in general carried out in the temperature range from 50 to 250°C, preferably from 60 to 150°C. The polymerisation can be carried out here continuously or batchwise.

The polymerisation is in general carried out in the presence of initiators, such as sensitisers or agents which form free radicals.

The initiators are in general employed in an amount of 0.01 to 3% by weight, preferably 0.1 to 1.5% by weight, based on the total monomer.

Polymerisation initiators which can be used are, for example, percompounds or azo compounds which supply free radicals. Examples which may be mentioned are:

aliphatic azodicarboxylic acid derivatives, such as azobisisobutyronitrile or azodicarboxylic acid esters, peroxides, such as lauroyl peroxide, succinyl peroxide, dibenzoyl peroxide, p-chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide and peroxides such as methyl ethyl ketone peroxide, methyl isobutyl ketone peroxide, cyclohexanone peroxide or acetylacetone peroxide, alkyl esters of peracids, such as tert.-butyl perpivalate, tert.-butyl peroctoate, tert.-butyl perbenzoate, tert.-butyl perisonononate, mono-tert.-butyl permaleate and tert.-butyl peracetate, percarbonates, such as dicyclohexyl and

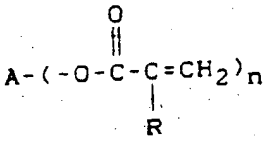
diisopropyl percarbonate, dialkyl peroxides, such as di-tert.-butyl peroxide and dicumyl peroxide, hydroperoxides, such as tert.-butyl hydroperoxide or cumene hydroperoxide, isophthalic mono-peracid or acetylcyclohexanesulphonyl peroxide.

A suspension of the filler is in general formed during the polymerisation. The filler can be isolated, for example, by evaporation of the solvent, for example in a spray drying process.

Component (b)

(Meth)acrylic acid esters which can form crosslinkings in general contain 2 or more polymerisable active groups, for example double bonds or isocyanate groups, in the molecule. Esters of (meth)acrylic acid with alcohols which are 2- to 5-valent and have 2 to 30 carbon atoms may be mentioned as preferred. Epoxide methacrylates and urethane methacrylates are particularly preferred.

Examples which may be mentioned are (meth)acrylic acid esters of the formula



in which

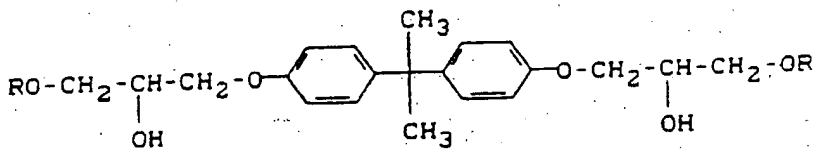
A denotes a straight-chain, branched or cyclic, aliphatic, aromatic or mixed aliphatic-aromatic

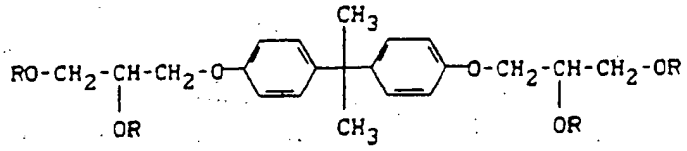
radical having 2 to 25 C atoms, which can be interrupted by -O- or NH bridges and substituted by hydroxyl, oxy, carboxyl, amino or halogen,

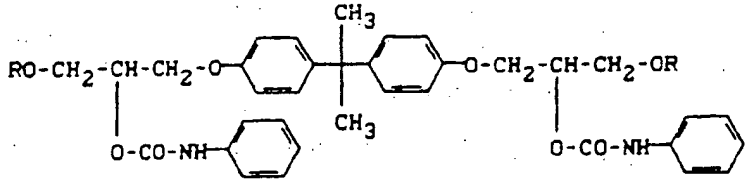
R denotes H or methyl and

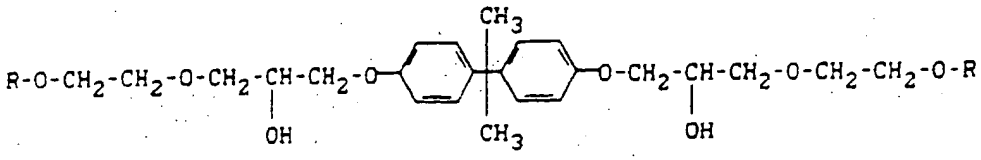
n represents an integer from 2 to 8, preferably 2 to 4.

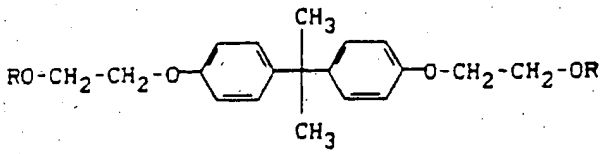
Compounds of the following formulae may be mentioned as preferred:

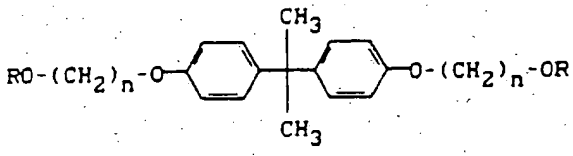


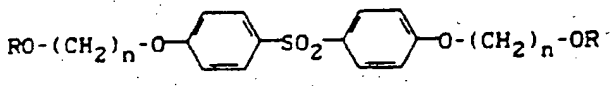


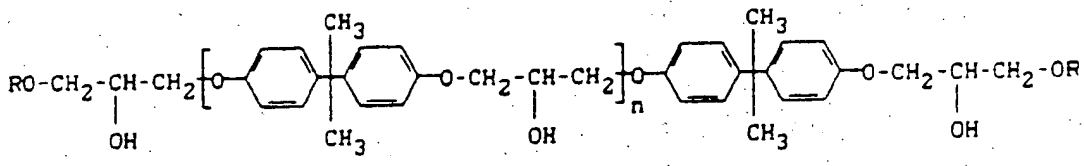


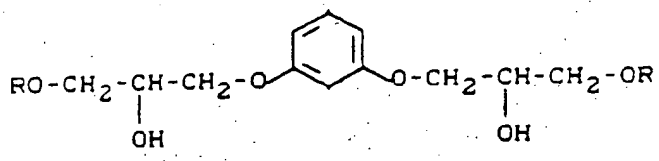


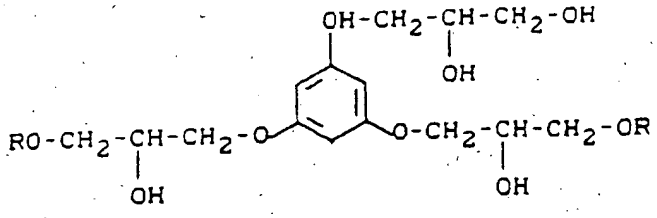


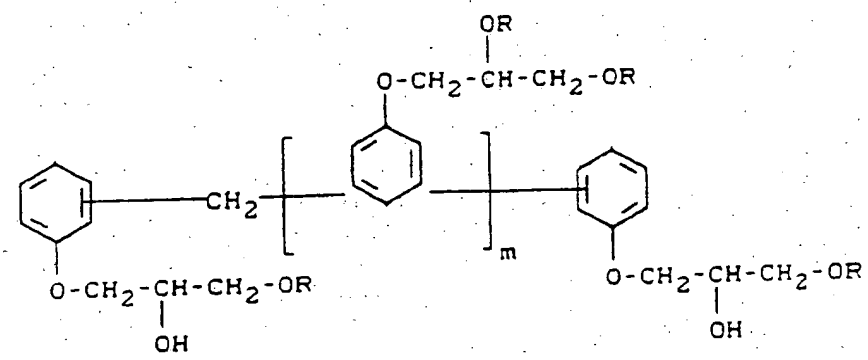


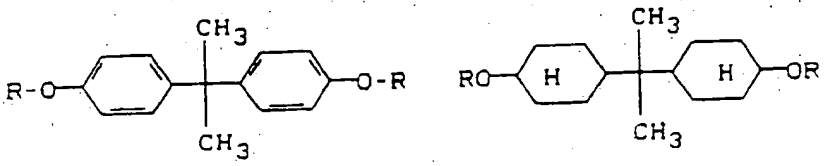


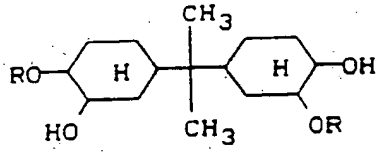


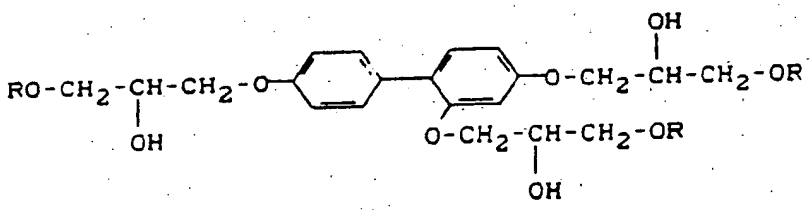


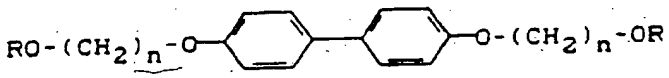


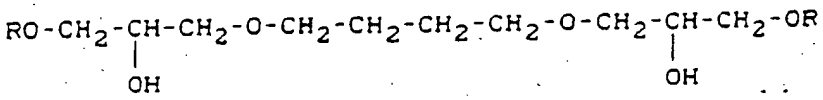


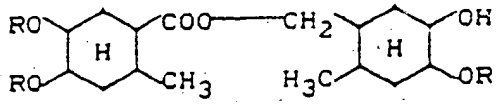


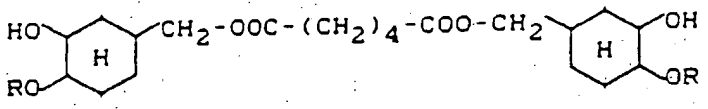


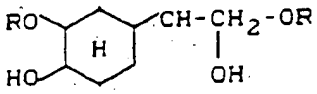


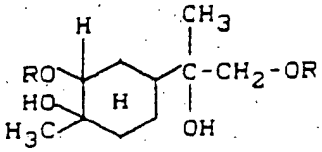


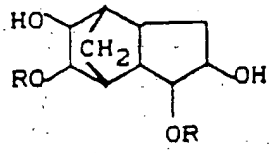


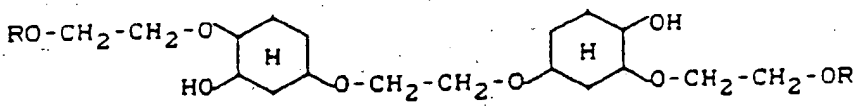


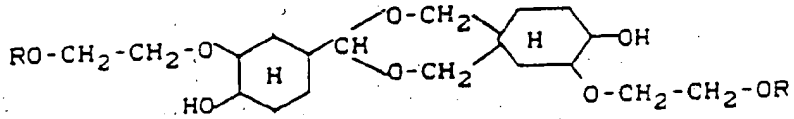


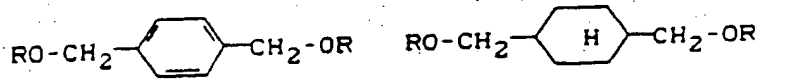


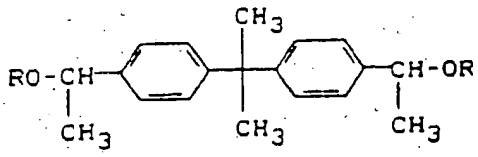


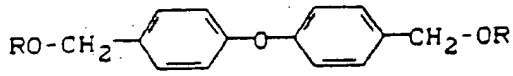


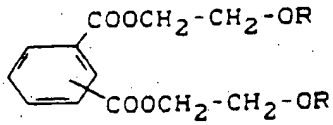




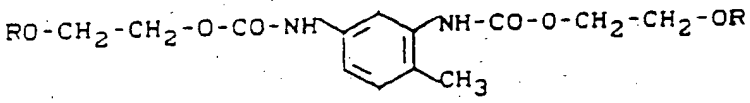


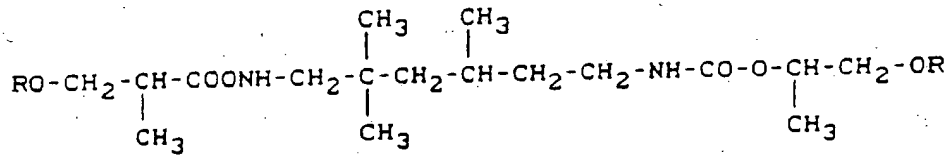


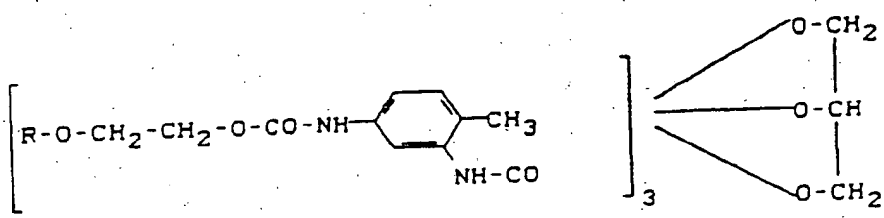




in the ortho, meta or para form







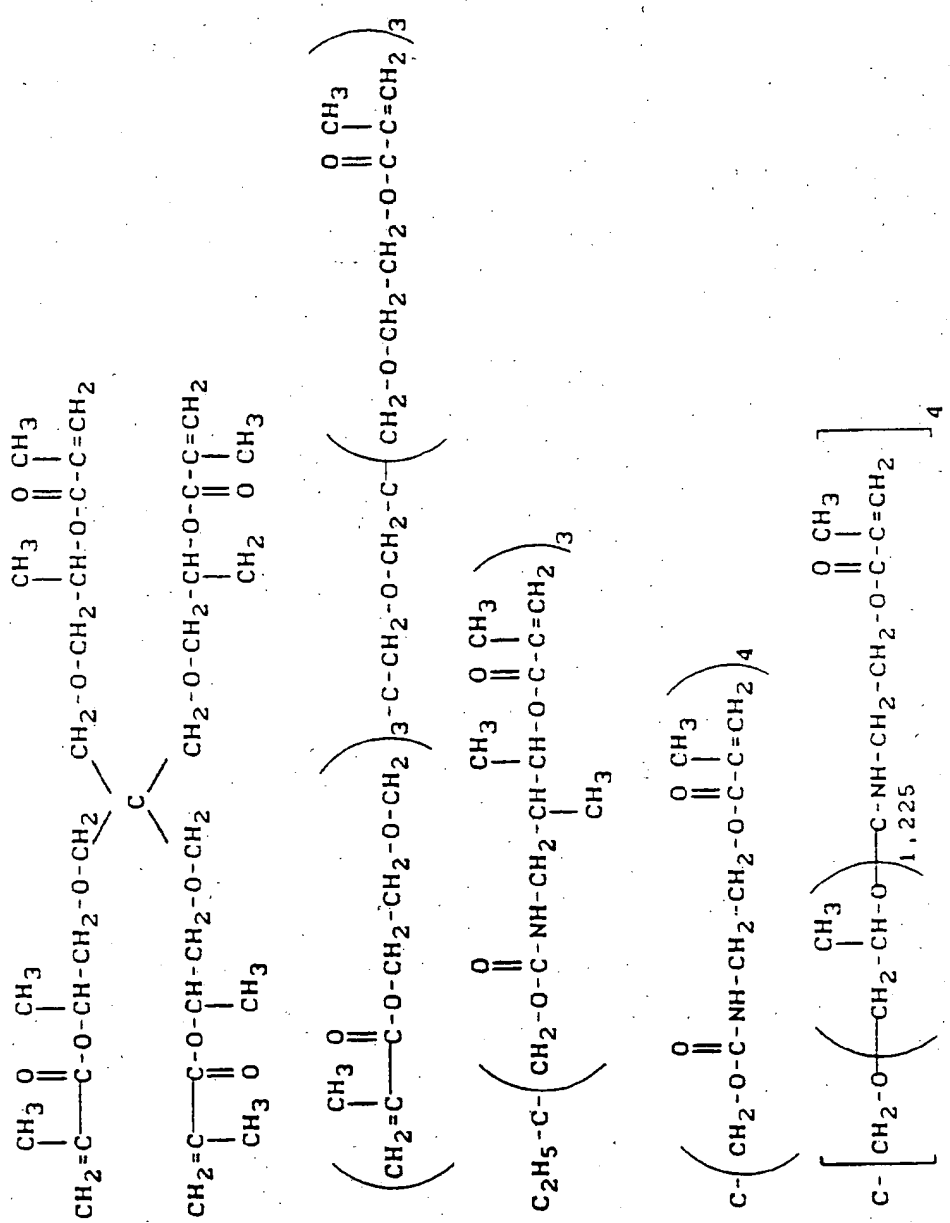
wherein

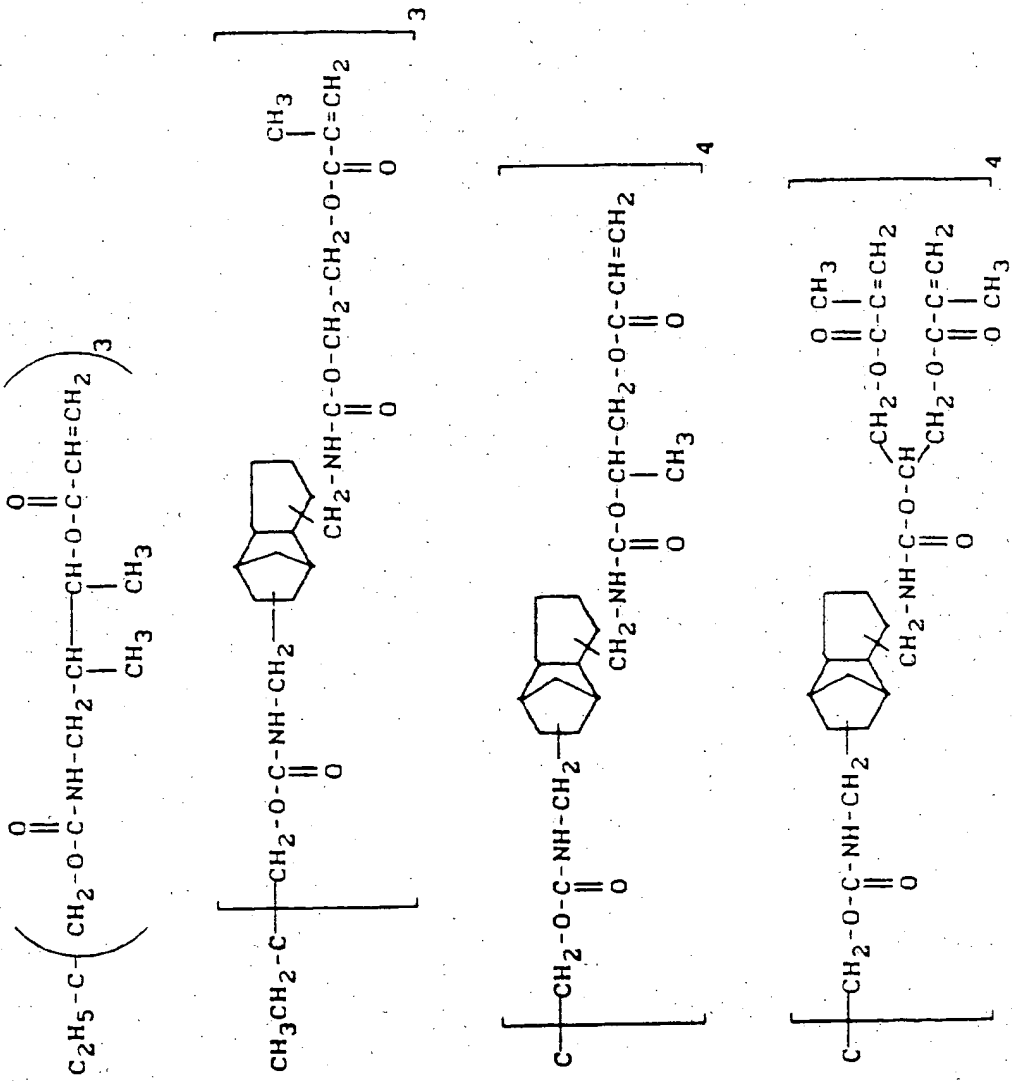
R represents $CH_2=C(CH_3)-C(=O)-$ or $CH_2=CH-C(=O)-$,

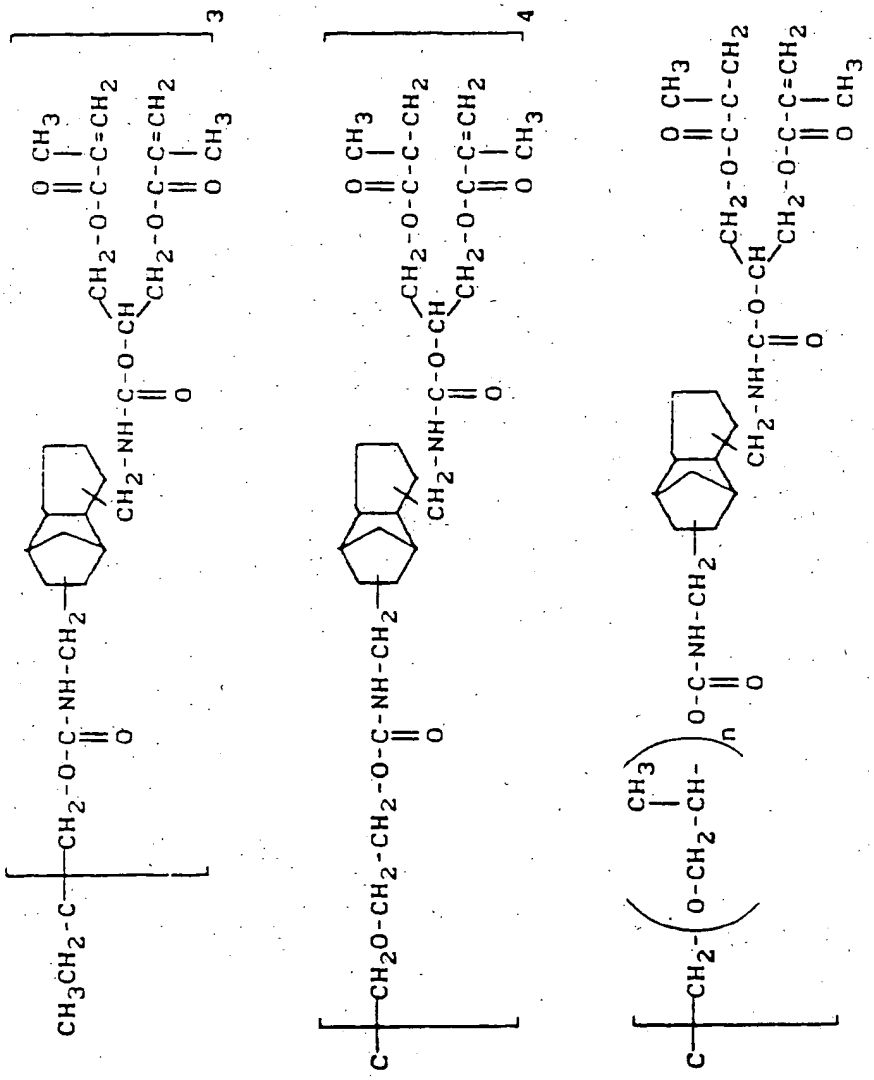
n denotes a number from 1 to 4 and

m denotes a number from 2 to 5.

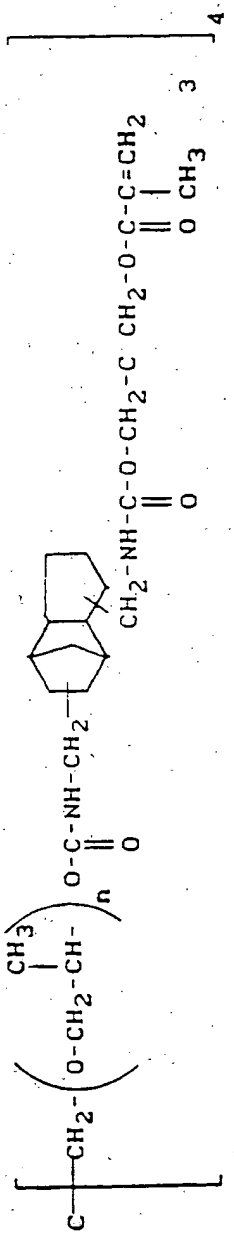
Derivatives of tricyclodecane (EP-A 0,023,686) and reaction products of polyols, diisocyanates and hydroxyalkyl methacrylates (DE-A 3,703,120, DE-A 3,703,080 and DE-A 3,703,130) may also be mentioned. The following monomers may be mentioned as examples:







n = 1.225 (statistical mean for 4 chains)



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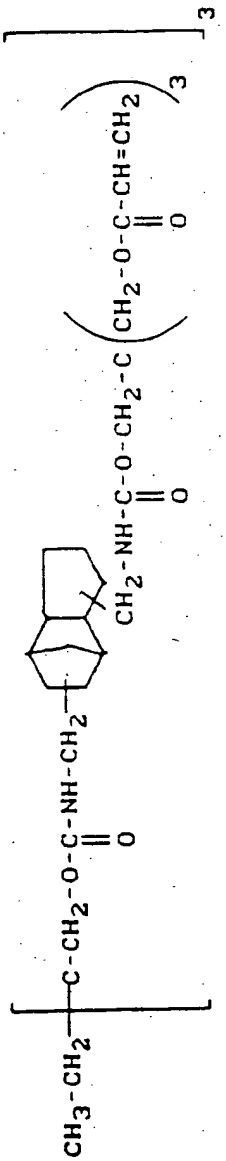
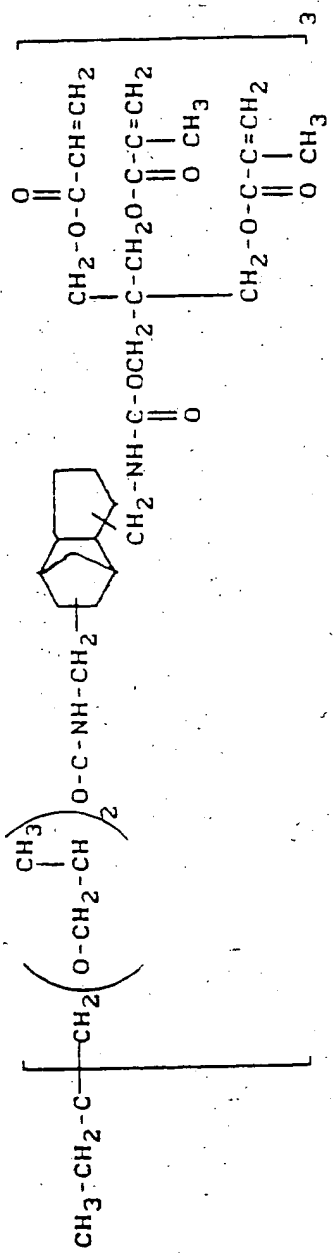
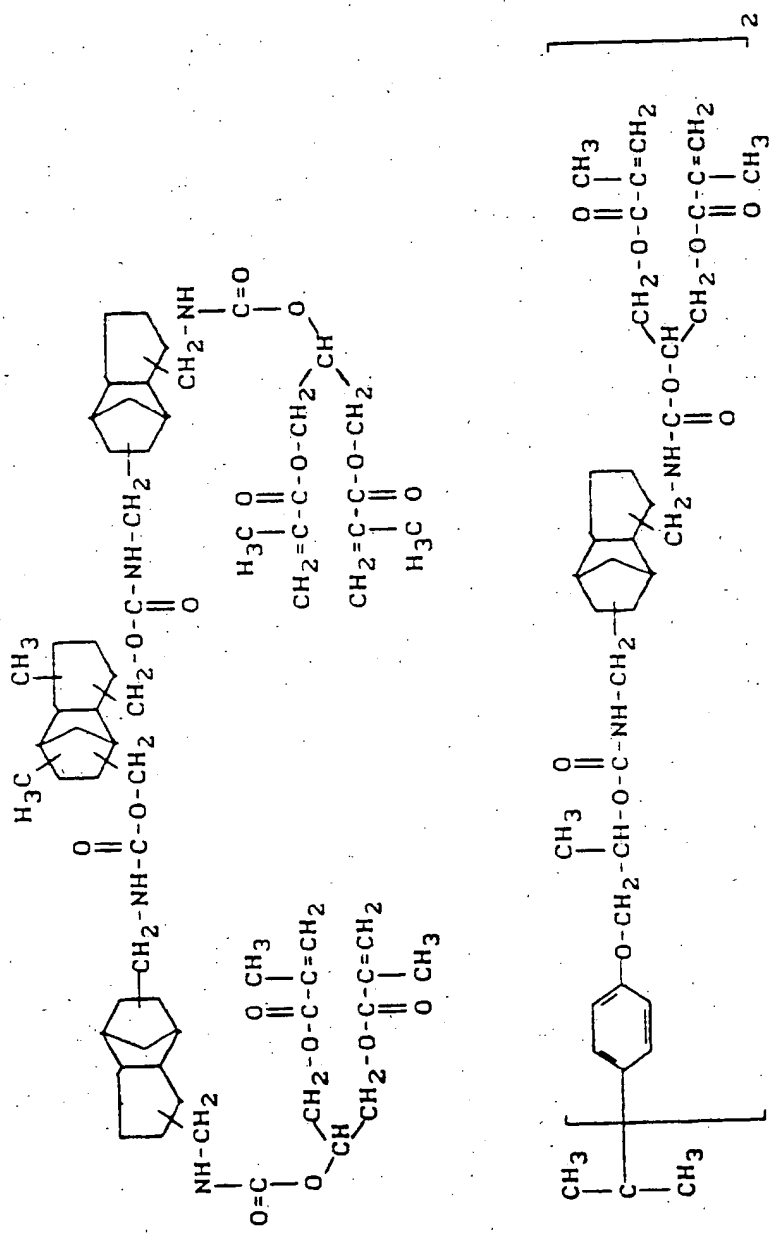
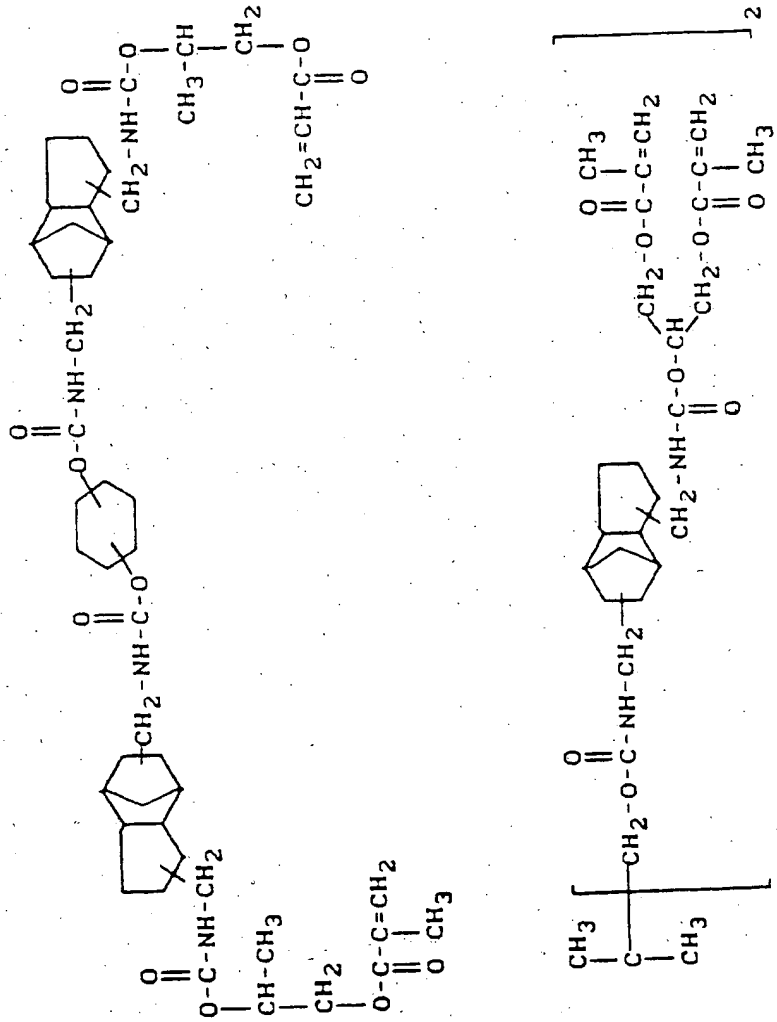
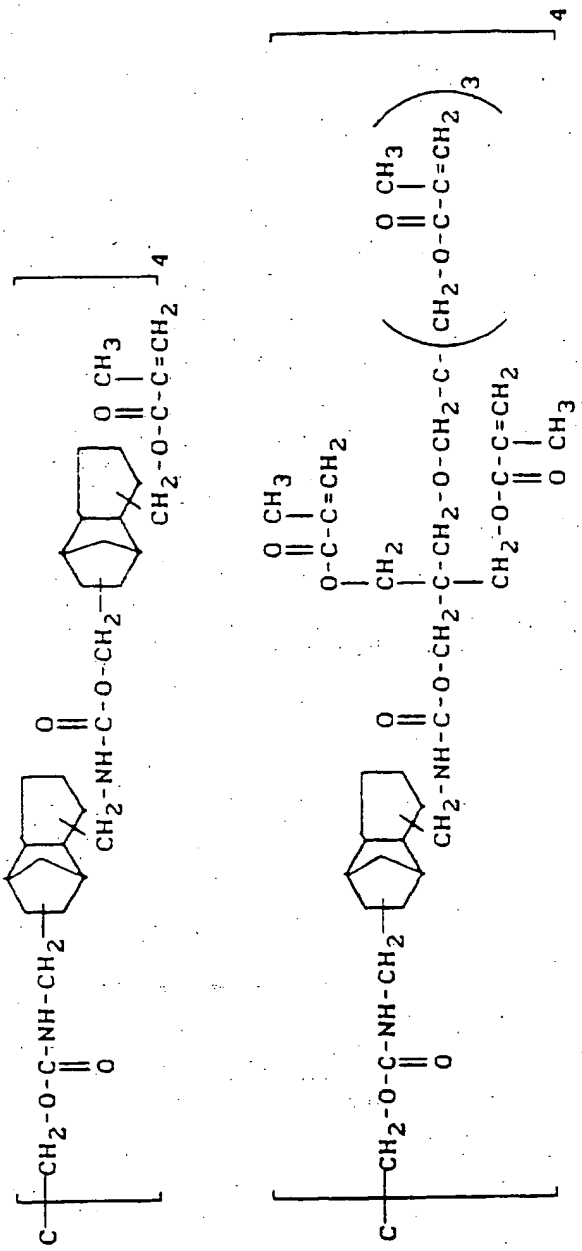
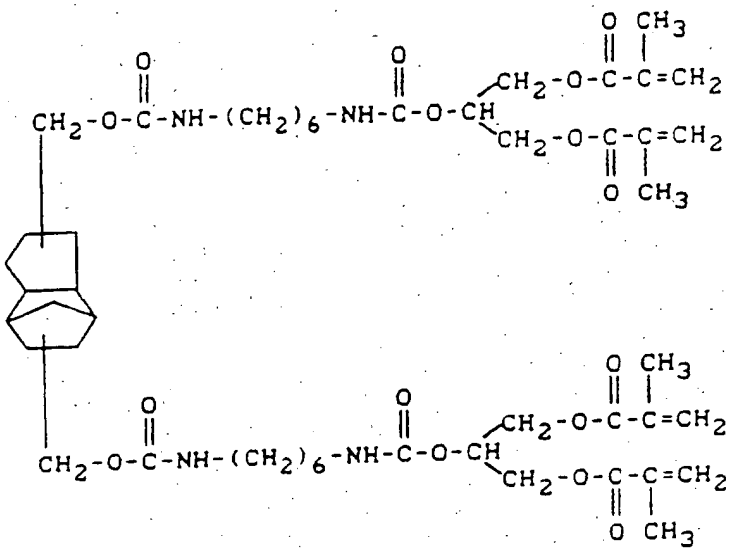


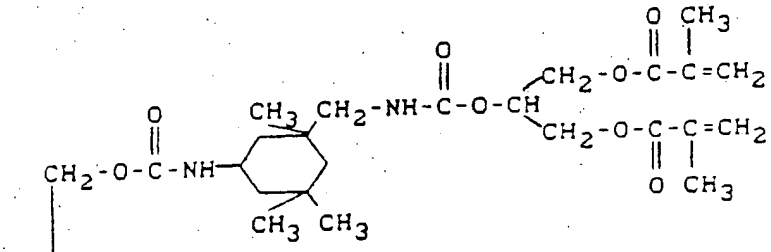


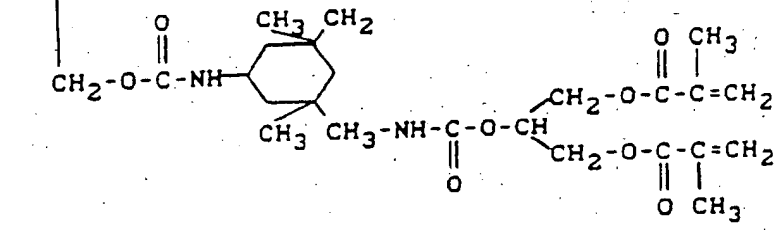


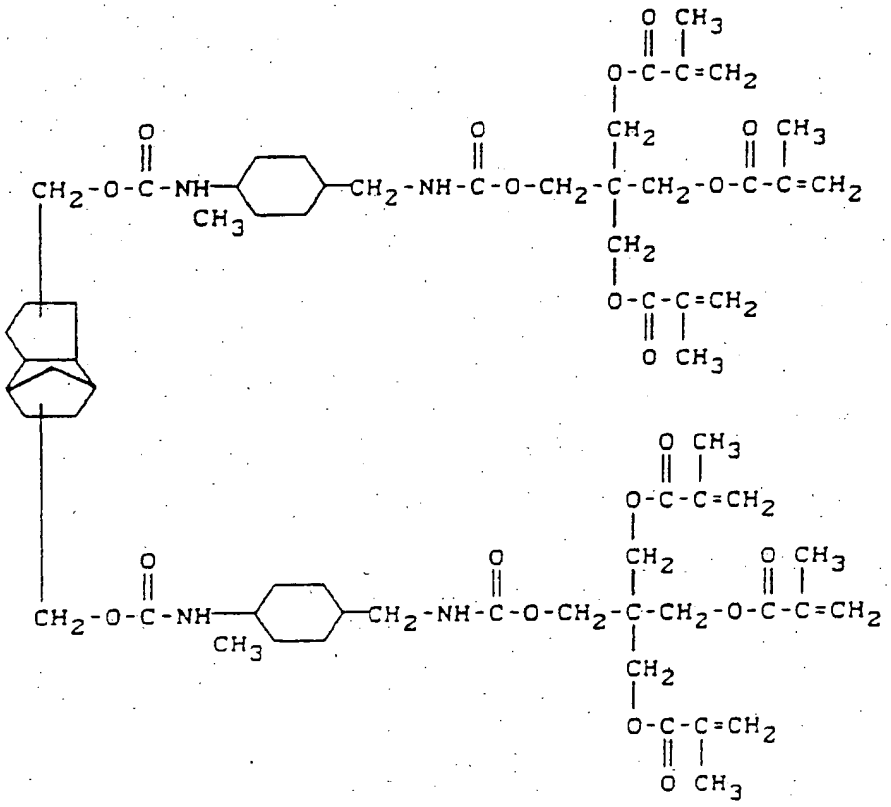


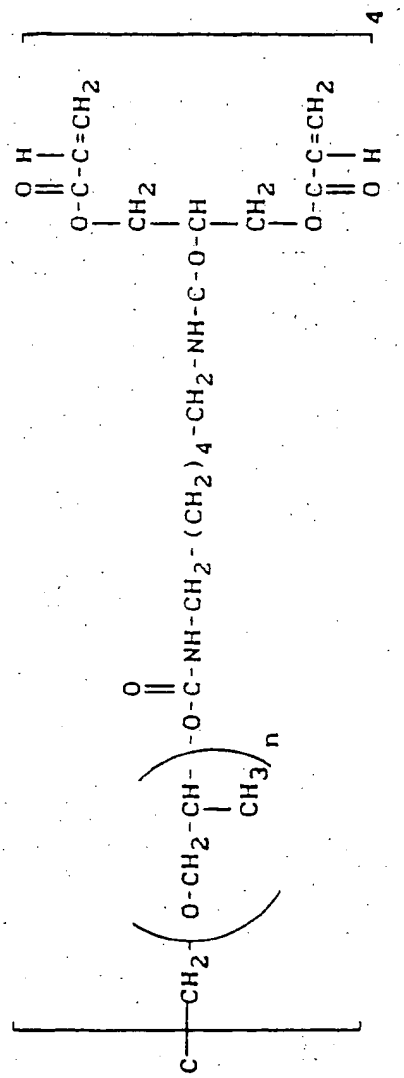




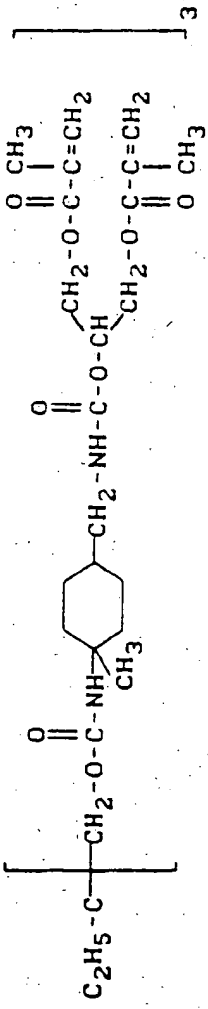








n = 1.225 (statistical mean for 4 chains)



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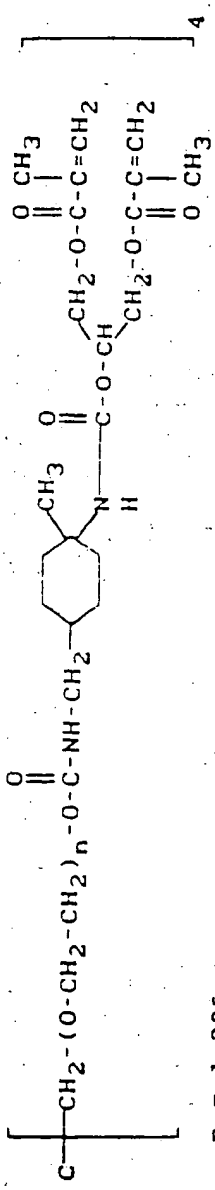
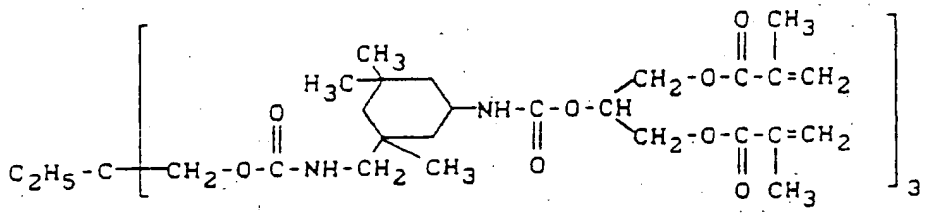
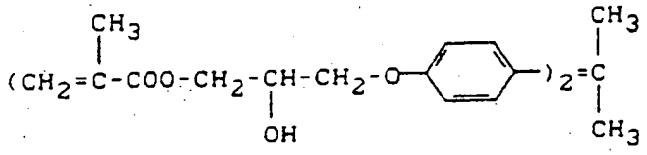


n = 1.225 (statistical mean for 4 chains)



So-called bis-GMA of the formula



is the particularly preferred monomer.

It is of course possible to employ mixtures of the various (meth)acrylic acid esters which can form cross-linkings. Examples which may be mentioned are mixtures of 20 to 70 parts by weight of bis-GMA and 30 to 80 parts by weight of triethylene glycol dimethacrylate.

Component (C)

(Meth)acrylic acid esters which cannot form crosslinkings are in general monofunctional (meth)acrylates. Examples which may be mentioned are C_1-C_{12}-, preferably C_1-C_4-alkyl methacrylates, such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, i-propyl methacrylate, n-butyl methacrylate and tert.-butyl methacrylate, hydroxyalkyl methacrylates, such as 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, diethylene glycol monomethacrylate and triethylene glycol monometh-

acrylate, and alkoxyalkyl methacrylates, such as 2-methoxyethyl methacrylate, 3-methoxybutyl methacrylate and ethyltriglycol methacrylate.

Preferred (meth)acrylic acid esters which cannot form crosslinkings are methyl methacrylate, ethyl methacrylate and hydroxyethyl methacrylate.

Components (b) and (c) as a mixture are in general employed as the monomer mixture for the dental materials according to the invention. These mixtures preferably have a viscosity in the range from 50 to 5000 mPa.s, preferably in the range from 100 to 2000 mPa.s (in each case at 20°C).

Component (d)

The inorganic fillers can consist, for example, of spherical or approximately spherical particles or regularly or irregularly shaped particles produced by grinding or directly by their preparation (for example prepared in a flame hydrolysis process). The inorganic fillers can be employed with a monomodal, bimodal or polymodal particle size distribution. The fillers in general have a maximum in the distribution curve in the range from 0.005 to 5 μm. Examples of suitable inorganic fillers are glass in the form of beads or in the form of irregularly shaped particles obtained by grinding having average particle sizes in the range from 0.5 to 5 μm. Oxides of silicon and aluminium which are obtained by flame hydrolysis and have particle sizes in the range

from 5 to 500 nm are furthermore suitable. The BET surface area of the inorganic fillers is 20 to 600 m^2/g, preferably 50 to 300 m^2/g. The inorganic fillers are employed in a form treated with adhesion promoters.

Examples of suitable adhesion promoters are silane compounds and titanate compounds, such as trimethylchlorosilane, hexamethyldisiloxane, 3-aminopropyltrimethoxysilane, butyl titanate and isopropyl titanate. Adhesion promoters having polymerisable groups, such as vinyltrimethylsiloxane, allyltrimethoxysilane and γ-methacryloyloxypropyltrimethoxysilane, are particularly suitable.

The after-treatment of the fillers is known per se. The treatment with silane compounds is advantageously carried out in a non-aqueous solvent, such as toluene, methylcyclohexane, acetone, tetrahydrofuran or methyl ethyl ketone, the reaction being catalysed with acids or amines.

The suitable amount of adhesion promoters depends on the size of the surface area of the inorganic filler. An amount of 0.5 to 5% is in general particularly suitable.

Component (e)

The dental materials according to the invention can contain additives which are known per se. Additives which may be mentioned are starter additions, stabilisers, pigments, dyestuffs, light stabilisers, fluorescence

agents or plasticisers.

Starter systems which are known per se (literature: Houben Weyl, Methoden der organischen Chemie (Methods of Organic Chemistry) Volume E20, page 15 et seq., Georg Thieme Verlag, Stuttgart 1987) can be used as starter additions for initiating the polymerisation. These are systems which produce free radicals, anions or cations and can trigger off free radical, anionic or cationic polymerisation. In the case of systems which produce free radicals, peroxides or aliphatic azo compounds, for example benzoyl peroxide, lauryl peroxide or azoisobutyrodinitrile, are particularly suitable; the systems are usually employed in amounts of 0.1 to 5% by weight. While the hardening can be carried out at elevated temperature by peroxides or other free radical initiators alone, an addition of accelerators, preferably aromatic amines, is in general advantageous for hardening at room temperature. Suitable accelerators are, for example, N,N-substituted toluidines and xylidines, such as N,N-dimethyl-p-toluidine or N,N-bis-(2-hydroxy-ethyl)-xylidine. The hardening can in general be achieved by addition of 0.5 to 3% by weight of the amines mentioned.

However, it is also possible to prepare dental materials which polymerise under the action of light, for example UV light, visible light or laser light. Photopolymerisation initiators and accelerators are employed in these cases.

Photopolymerisation initiators are known per se (literature: Houben Weyl, Methoden der organischen Chemie (Methods of Organic Chemistry), Volume E20, page 80 et seq., Georg Thieme Verlag Stuttgart 1987). They are preferably carbonyl compounds, such as benzoin and derivatives thereof, in particular benzoin methyl ether, benzoyl and benzyl derivatives, for example 4,4-oxydibenzyl, and other dicarbonyl compounds, such as thiacetyl, 2,3-pentadione or metal carbonyls, such as pentacarbonylmanganese, and quinones, such as 9,10-phenanthrenequinone and camphorquinone, or derivatives thereof.

The content of such photopolymerisation initiators is preferably about 0.01 to about 5% by weight of the total composition.

The photopolymerisable compositions which can be hardened by light preferably also contain substances which accelerate the polymerisation reaction in the presence of photopolymerisation initiators. Examples of known accelerators are aromatic amines, such as p-toluidine and dimethyl-p-toluidine, trialkylamines, such as trihexylamine, polyamines, such as N,N,N',N'-tetraalkylalkylenediamine, barbituric acid and dialkylbarbituric acid and sulphimides.

The accelerators are in general employed in an amount of 0.01 to about 5% by weight of the total mixture.

It is also possible to add UV stabilisers to the dental

materials according to the invention in order to avoid after-darkening during ageing.

2-Hydroxy-4-methoxybenzophenone is a particularly suitable UV stabiliser. Another preferred material is 2-(2'-hydroxy-5-methylphenyl)-benzotriazole. Hydroquinone, p-benzoquinone and p-butylhydroxytoluene may also be mentioned as examples.

The dental materials according to the invention can also contain pigments and dyestuffs which are known per se in order to establish a colour which is as true to nature as possible.

The polymerisation is in general carried out under the abovementioned conditions.

The dental materials according to the invention can be processed, with shaping, to give false teeth and dental prostheses, such as crowns, bridges, inlays and overlays, and to give tooth fillings and dental varnishes. The polymerised dental materials according to the invention are distinguished by a favourable combination of properties. They have a good hardness, a high rigidity and a high abrasion resistance, coupled with a good toughness. They can easily be coloured and matched to the natural tooth colour.

Example 1

Preparation of a polymethacrylic acid ester from ethylene glycol dimethacrylate

1800 g of 2-butanone, 200 g of ethylene glycol dimethacrylate and 2 g of dibenzoyl peroxide are weighed into a 3-litre glass reactor fitted with a blade stirrer, reflux condenser, internal thermometer, gas inlet and gas outlet tube. The mixture is heated under reflux for 2 hours, while stirring at 300 revolutions per minute and flushing with nitrogen. An easily stirrable suspension is formed. 190 g of fine powder can be obtained from this by spray drying. The average particle size (measured by laser correlation spectroscopy) is 700 nm, the gel content is 98.4% and the degree of swelling (measured in tetrahydrofuran) is 310%.

Example 2

Preparation of a polymethacrylic acid ester from glycerol dimethacrylate

500 g of glycerol dimethacrylate and 5 g of dibenzoyl peroxide were reacted in 2000 g of 2-butanone by the procedure described in Example 1. 475 g of powder having a particle size of 350 nm, a gel content of 97.3% and a degree of swelling of 280% were obtained.

Example 3

Polymerisable composition

25 g of polymer from Example 1, 65 g of bis-GMA, 35 g of triethyleneglycoldimethoacrylate, 40 g of microfine silicon dioxide (having a BET surface area of 130 m^2/g, silanised with 5% of γ-methacryloyloxypropyltrimethosilane) and 0.4 g of dibenzoyl peroxide are kneaded in a laboratory kneader for 30 minutes. The resulting composition is kept at 35°C for 5 hours. A non-tacky, transparent, doughy paste is obtained.

Example 4

Polymerisable composition

20 g of polymer from Example 1, 65 g of bis-GMA, 35 g of triethyleneglycoldimethacrylate, 50 g of microfine silicon dioxide (having a BET surface area of 90 m^2/g, silanised with 3% of γ-methacryloyloxypropyltrimethosilane) and 0.4 g of dibenzoyl peroxide are kneaded in a laboratory kneader for 30 minutes. The resulting composition is stored at 35°C for 5 hours. A non-tacky, transparent, doughy paste is obtained.

Example 5

The compositions from Examples 3 and 4 and 3 comparison materials were polymerised at 140°C under 200 bar in the

course of 10 minutes to give a test sheet. Values for the flexural strength in accordance with DIN 13 922 and the flexural E modulus in accordance with DIN 13 922 as well as the penetration depth according to Wallace were determined.

The Wallace method is used to determine the indentation hardness on plastics. A Vickers diamond is applied to the surface under a preload of 1 p and then subjected to a main load of 100 p for 60 seconds. The penetration depth of the diamond under the main load is measured as a measure of the penetration resistance. In contrast to the Vickers or Brinell hardness measurements, in which the test force is based on the dimension of the permanent indentation, the Wallace method determines the elastic and permanent deformation of the plastic.

	Flexural strength N/nm^2	E modulus N/nm^2	HW μm
Example 3	138 ± 11	5200 ± 160	15.2
Example 4	146 ± 6	5400 ± 120	14.8
customary PMMA system	112 ± 9	2800 ± 100	22.8 ± 1.5
US 4,396,377 Example 1	118 ± 10	3050 ± 80	20.3 ± 1.1
EP-A-110,092 Example 3	140 ± 7	3800 ± 150	16.2 ± 0.9

Patent Claims

1. Dental materials containing

a) 5 to 30 parts by weight of an organic filler consisting of polymeric crosslinked (meth)-acrylates having a particle size in the range from 0.001 to 100 µm, a degree of swelling of 50 to 2000% by weight and a degree of cross-linking of 1 to 100% by weight, in each case based on the polymer,

b) 40 to 80 parts by weight of (meth)acrylates which can form crosslinkings,

c) 0 to 40 parts by weight of (meth)acrylates which cannot form crosslinkings,

d) 10 to 40 parts by weight of a silanised inorganic filler having an average particle size of 0.005 to 5 µm and

e) 0.1 to 10% by weight of one or more additives.

2. Dental materials according to Claim 1, characterised in that the organic filler has a BET surface area of 20 to 600 m^2/g.

3. Dental materials according to Claims 1 and 2, characterised in that the inorganic filler has a BET

surface area of 50 to 250 m^2/g.

4. Dental materials according to Claims 1 to 3, characterised in that the mixture of (meth)acrylic acid esters which can form crosslinkings and cannot form crosslinkings has a viscosity in the range from 50 to 5000 mPa.s.

5. Process for the preparation of dental materials, characterised in that a mixture of

a) 5 to 30 parts by weight of an organic filler consisting of polymeric crosslinked (meth)-acrylates having a particle size in the range from 0.001 to 100 µm, a degree of swelling of 50 to 2000% by weight and a degree of crosslinking of 1 to 100% by weight, in each case based on the polymer,

b) 40 to 80 parts by weight of (meth)acrylates which can form crosslinkings,

c) 0 to 40 parts by weight of (meth)acrylates which cannot form crosslinkings and

d) 10 to 40 parts by weight of a silanised inorganic filler having an average particle size of 0.005 to 5 µm

is polymerised.

6. Use of polymerised dental materials according to Claims 1 to 4 as false teeth, dental prostheses, tooth-fillings and dental varnishes.

7. A dental material according to claim 1, substantially as hereinbefore described and exemplified.

8. A process for the preparation of a dental material according to claim 1, substantially as hereinbefore described and exemplified.

9. A dental material according to claim 1, whenever prepared by a process claimed in a preceding claim.

10. Use according to claim 6, substantially as hereinbefore described.

Dated this the 13th day of March, 1992

F. R. KELLY & CO.

BY: _____ EXECUTIVE

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AGENTS FOR THE APPLICANTS